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SECURITY DOCUMENT INCLUDING A NANOPARTICLE-BASED
AUTHENTICATION DEVICE

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The present invention relates to security documents such as banknotes,
5 credit cards and other documents of value, and is particularly concerned with
providing a security document with an authentication device for verifying the
authenticity of the security document. The invention is also concerned with a
method of producing such security documents.

The counterfeiting of currency, stocks, bonds, credit cards and other
10 valuable documents essential to conduct business and financial activities is a
continuing serious problem. The widespread availability of high quality imaging
systems and the increasing technological sophistication of counterfeiters increases
the difficulty of combatting all forms of counterfeiting.

Currently, considerable resources are devoted to the development of
15 devices for incorporation into a security document which can be detected to
validate the document's authenticity. Holograms, opaque print strips and
microprinting are examples of such devices, and their effectiveness depends upon
the difficulties involved in counterfeiting them.

An aim of the present invention is to provide an authentication device for
20 incorporation in a security document which acts to effectively circumvent
counterfeiting of the security document.

With that in mind, one aspect of the present invention provides a security
document comprising a sheet-like substrate having one or more layers containing
solid inorganic particles of controlled shape for forming an authentication device
25 in a first location on the security document, the particles having at least a first
dimension in the range of 1 to 200 nanometers.

The particles may be substantially spherical. In another embodiment, the
particles may be elongated. In a third embodiment, the particles may be a series
of spherical particles concatenated together, in the form of "beads-over-string". In
30 the case of elongated particles, at least a first group of the particles may be aligned
so that their longitudinal axes are substantially parallel. The longitudinal axis of

the first group of particles may extend in a first direction at an angle to the plane of the security document.

A second group of the particles may be aligned so that their longitudinal axes extends in a second direction at an angle to the plane of the security document, the first and second directions being non-co-linear.

The first group of particles may be arranged so as to polarize incident light waves. In one embodiment, the security document may include, at a second location, a polarizing analyzer for interaction with the light polarizer at the first location.

The particles may be laterally spaced from each other so as to form at least a first diffraction grating at the first location. The lateral spacing may be achieved by coating each particle with a transparent material of controllable thickness, such as silica.

The particles may be selected from materials which reflect incident light waves. Alternatively, the particles may act to fluoresce or luminesce light waves therefrom.

In a further embodiment of the invention, the particles may be selected from materials to reflect incident sound or acoustic waves or from materials that absorb energy (light or sound) and subsequently re-emit this energy acoustically.

The particles may be made from material which is orientable in an electric, magnetic or electromagnetic field. In this way, alignment of the particles may be affected by selective application of that specified field to at least the first group of particles.

Another aspect of the present invention provides a method of producing a security document, comprising the steps of:

(a) forming a sheet-like substrate having one or more layers containing particles for forming an authentication device at a first location on the security document, the particles having at least a first dimension in the range of 1 to 200 nanometers,

(b) melting at least a portion of the first layer such that the particles can orient under the influence of external field,

- (c) applying the external field so as to orient the particles,
- (d) allowing the first layer to cool so as to fix the orientation of the particles.

The external field may be for example an electric, magnetic,
5 electromagnetic, mechanically induced stress field.

A further aspect of the present invention provides a method for producing a security feature for use in a security document, comprising the steps of:

- (a) forming a sheet-like substrate,
- (b) producing pores in an outer layer of the substrate at regular
10 intervals, the pores having a pre-determined alignment with each other, and
- (c) depositing particles in the pores, the particles having at least a first dimension in the range of 1 to 200 nanometers

The particles may be deposited by an electro-deposition process. The outer layer may be made from a polymer-based material.

- 15 The pores may be formed by orienting the substrate so that its plane is at an angle to the beam of an energy source, exposing the substrate to the energy source beams such that pores are formed in an outer layer of the substrate, the longitudinal axis of the pores being substantially aligned with the direction of the energy source beam.

20 Yet another aspect of the present invention provides a method of producing a security document, comprising the steps of:

- (a) forming a sheet-like substrate,
- (b) placing particles for forming an authentication device on a transfer film, the particles having at least a first dimension in the range of 1 to 200
25 nanometers, and
- (c) using a die to cause the transfer film to press the particles into the substrate.

The die may be heated so that an outer layer of the substrate is melted thereby to facilitate the transfer of the particles from the transfer film into the
30 substrate.

The die may be an embossing die and may be adapted to form a saw-tooth or like profile in the surface of the substrate, in order to enable the positioning of the particles in the outer layer of the substrate, whereby the longitudinal axis of the particles is at an angle to the plane of the security document.

5 A further aspect of the invention provides a method of producing a security document, comprising the steps of:

- (a) forming a sheet-like substrate,
- (b) coating at least a first outer surface of the substrate with a layer containing spherical particles having a diameter in the range of 1 to 200
10 nanometers,
- (c) heating at least one or more selected portions of the layer to allow the spherical particles to self-assemble into a concatenated series within said at least one of more selected areas.

In order that the present invention may be more readily understood, various
15 embodiments thereof will be now described, by way of example only, with reference to the accompanying drawings.

In the drawings:

Figure 1 is a cross-sectional side view of a first embodiment of a security document according to the present invention;

20 Figure 2 is a cross-sectional side view of a second embodiment of a security document according to the present invention;

Figure 3 is a perspective view of the security document of Figure 2;

Figure 4 is a diagram showing the spectral absorption of particles for use in a security document according to the present invention;

25 Figure 5 is a schematic diagram showing the orientation of the particles used in the security document of Figure 2;

Figures 6 and 7 are cross-sectional side views of a third embodiment of a security document according to the present invention;

Figures 8 and 9 are schematic representations of portions of the security
30 document of Figures 6 and 7;

Figure 10 is a schematic plan view showing a lined particle suitable for use in a security document according to the present invention;

Figure 11 is a schematic plan view of particles encapsulated in a clear transparent material for use in a security document according to the present invention;

Figure 12 is a cross-sectional side view of a fourth embodiment of a security document according to the present invention;

Figure 13 is a cross-sectional side view of a fifth embodiment of a security document according to the present invention;

Figure 14 is a schematic diagram showing a first method of locating particles in a substrate so as to form a security document according to the present invention; and

Figure 15 is a schematic diagram showing a second method for enabling the location of particles in a substrate so as to form a security document according to the present invention.

Referring now to Figure 1, there is shown generally a banknote 1 comprising a sheet-like substrate 2 preferably of plastics material and having first and second opposing surfaces 3 and 4. Various indicia may be formed on at least one of the first and second opposing surfaces 7 and 8, such as drawings, writing and other designs well known to manufacturers and users of banknotes.

The substrate is preferably a composite made from at least biaxially oriented polymeric film 5 which is coated on both sides with an opacifying pigmentary coating 6 and 7 comprising a major portion of pigment in a minor portion of cross-linked polymeric binder. A transparent protective coating (not shown) is preferably applied to both sides of the banknote 1 in order to protect it from wear. The transparent protective layer may include silica or like particles so as to improve the adherence of the banknote 1 when handled by a user.

The substrate 2 includes copolymer outer coatings 8 and 9 of the biaxially oriented polymeric film 5. An authentication device 10 is formed at a first location on the banknote 1 by the inclusion of nanoparticles of controlled shape in at least a portion of the copolymer outer coating 8. These nanoparticles have at least a first dimension

in the range of 1 to 200 nanometers, and, when included in a security document, provide a number of features suitable for use as an authentication device, as will be explained below.

ART 34A(1)
The opacification layer 6 of the banknote 1 does not extend over the entire surface 3 of the substrate 2, but leaves a portion of the substrate 2 uncovered in the vicinity of the authentication device 10. This embodiment of the authentication device 10 takes advantage of particular optical effects of the nanoparticles included in the copolymer outer layer 8 or otherwise visible by a user. In this example, nanoparticles made from gold, silver or other solid inorganic material which scatters and absorbs incident light waves are used in the authentication device 10. Nanoparticles of this type have been observed to exhibit isotropic absorption of incident light waves, their absorption spectrum being a function of both their aspect ratio, that is to say the ratio of their length to width, and their orientation. The absorption spectra for such nanoparticles in solution each having the same width of 10 nanometers but having different lengths is shown in Figure 4. It has been observed that the short-axis polarized band, indicated by the reference "S" does not change in position, whereas the long-axis polarized band, indicated by the reference "L", shifts to a longer wavelength as the length of the nanoparticles increases. In the simplest case, nanoparticles of a spherical shape may be used in the authentication device 10. Such gold nanospheres have been observed to exhibit a colour shift in reflection as a function of the viewing angle α . Such an authentication device will have a typical "green-golden" colour when viewed under specular reflection and appears red-crimson when viewed in diffuse reflectance. The actual "red-crimson" colour which is viewed in diffuse reflectance will depend upon the actual size of the nanosphere and on the thickness of any coating on it.

Alternatively, nanorods, nanoellipsoids or other elongated nanoparticles may be used in order to alter the colour observed by a user both under specular reflection and by diffuse reflectance of light on the surface of the authentication device 10.

The same nanoparticles have also been observed to exhibit a colour shift when viewed in transmission versus reflection. Figure 2 shows a banknote 20 which takes advantage of this property. The same substrate 2, including the biaxially oriented polymeric film 5 and copolymer outer coatings 8 and 9 are used.

5 However, the opacifying layers 6 and 7 do not entirely cover the outer surfaces 3 and 4 of the substrate, but leave open a region W enabling the transmission of light through the substrate 2. In this case, a colour difference is observed by a user depending upon whether light from a source 21 is viewed in reflection, at position 22, or in transmission, at position 23.

10 A variation in the colour observed by a user may also be achieved by the alignment of elongate nanoparticles in the authentication device 10. Alignment of at least a first group of the particles so that their longitudinal axes are substantially parallel results in not only a colour variation depending upon the angle α at which the banknote 20 is tilted, but which is also dependent upon an angle β at which the
15 banknote is rotated whilst being maintained in substantially the same plane.

If, as shown in Figure 5, the longitudinal axis of a first group of elongate nanoparticles are arranged to extend in a first direction at an angle to the plane of the security document, a noted colour variation depending upon the angle of rotation β of the banknote 20 is observed. In the example illustrated in Figure 5,
20 the group 30 of elongate particles have their longitudinal axes extending in a first direction indicated by the arrow 31 at an angle γ to the plane of the security document. In such a configuration, a shift in the absorption spectrum is observed by the viewer between the positions 32 and 33.

In other embodiments of the invention, a second or further groups of
25 particles may be aligned so that their longitudinal axes extend in a second direction, which is different from the direction indicated by the arrow 31, at an angle to the plane of the security document. In this way, various patterns may be observed by a viewer of the authentication device, the various portions of the pattern being formed by the various groups of aligned particles within the
30 authentication device. The various parts of the authentication device will exhibit a

viewed colour difference depending upon the orientation of the banknote 20 with respect to the viewer.

Whilst the nanoparticles used in the authentication device 10 of Figures 1 to 5 are adapted to reflect incident light waves, similar optical effects may be achieved with nanoparticles which act to fluoresce or luminesce light waves therefrom.

Referring now to Figure 6, there is shown a further embodiment of the present invention in which the optical effects of the nanoparticles arise from polarization of incident light. In this figure, the banknote 40 again includes a substrate 41 including a biaxially oriented polymeric film 42 and 2 copolymer outer coatings 43 and 44. Opacifying coatings 45 and 46 are formed on the outer surfaces of the copolymer outer coatings 43 and 44. An authentication device 47 is formed at a first location on the banknote 40. In this example, elongate nanoparticles are positioned within the copolymer outer coating 43 such that their longitudinal axes are substantially parallel with the plane of the banknote 40 and are aligned in a first selected direction. In the example shown, a window X is formed through the banknote 40 in the vicinity of the authentication device 47, by leaving that portion of the transparent substrate 41 uncoated by the opacifying coatings 46 and 45. The group of aligned nanoparticles located in the copolymer outer layer 43 forming part of the authentication device 47 cover only a portion Y of the width of the window X. Because the absorption spectrum of the nanoparticles is anisotropic, it may act as efficient light polarizers. They do this by selectively absorbing the plane of polarized light at a specific wavelength, as indicated in Figure 4. In this application there is no need to orient the elongate nanoparticles at an angle relative to the viewer and the elongate nanoparticles are simply laid down with their longitudinal axes parallel to the banknote surface.

Patterns may be formed within the window X by providing a further group or groups of elongate nanoparticles having their longitudinal axes aligned along a different direction to that of the first group of nanoparticles. For example, whilst a first group of nanoparticles 48 in the copolymer outer coating 43 may be oriented along a first direction, other groups 49 and 50 of elongate nanoparticles may be

formed in the opposing copolymer outer coating 44 in areas within the boundaries of the window X, but outside the boundaries of the first group of elongate nanoparticles Y. The latent image thus formed when the banknote is viewed in transmission is invisible as all the elongate nanoparticles have their longitudinal axis normal to the viewing direction, thus producing a uniform colour.

However, when an analyzer is interposed between the latent image and the viewer, extinction occurs where the long individual axes of the elongate nanoparticles are orthogonal. Conveniently, the analyzer may be provided at a second location on the banknote 40 so that, as seen in Figure 7, the banknote 40 may be folded so as to superpose the analyzer 51 and the polarizing authentication device 47. Alternatively, the analyzer may be provided on a separate document or device. For example, 2 banknotes or other security documents including the authentication device 47 may be used to verify each other.

The analyzer 51 is formed by locating elongate nanoparticles within a window Z of the banknote 40. The elongate nanoparticles in the analyzer 51 have their longitudinal axes aligned along a direction coincident with the direction along which one or more groups of particles forming part of the authentication device are aligned.

Figure 8 provides an illustration of this. In this example, the first group of elongate nanoparticles are located in the outer copolymer layer 43 with their longitudinal axes extending in the direction indicated by the arrow 52. The groups 49, 50 of elongate nanoparticles in the copolymer outer layer 44 have their longitudinal axes extending in the direction indicated by the arrow 53. When the window 47 of the banknote is examined by a user, the latent pattern or image formed by the groups 48 to 50 of elongate nanoparticles is not visible to the user. The elongate nanoparticles in the groups 48 to 50 are so disposed in the copolymer outer layers 43, 44 so as to polarized incident light waves. The group of elongate nanoparticles in the analyzer 51 have their longitudinal axes extending in the direction indicated by the arrow 53. When the two portions of the banknote 40 are superposed, as in Figure 7, extinction of image occurs where the longitudinal axis of the elongate nanoparticles in the analyzer 51 are orthogonal with the

longitudinal axes of the elongate nanoparticles in the group 48 of nanoparticles in the polarizer 47. The resultant exposed image is referenced 54.

Figure 9 schematically illustrates the fact that the group 48 of elongate nanoparticles may be applied to one outer layer of the banknote 40, whilst the groups 49, 50 may be applied to the opposing side of the banknote 40. In other embodiments, it is to be appreciated that one or more or all groups of nanoparticles forming such a pattern may be formed in an outer layer. In other embodiments of the invention, the nanoparticles may be located in the central polymeric film 42.

Once the previously described authentication devices relied upon the absorption spectrum of nanoparticles to produce a security optical effect, authentication devices including such nanoparticles may be created which rely upon the diffraction of incident light. If elongate nanoparticles are packed as shown in Figure 10, that is to say with their longitudinal axes aligned in the same direction but where the nanoparticles are not laterally spaced, no controllable diffraction effects result. However, if the elongate nanoparticles are arranged in an authentication device so that their longitudinal axes extend in the same direction and the spacing between the nanoparticles is controlled, then an authentication device exhibiting zero order diffraction effects may be produced. One way of achieving this effect is via the encapsulation of the elongate nanoparticles in a transparent material of controllable thickness, such as silica. The grating period in this case is equal to the width of the nanoparticle plus twice the wall thickness. Varying the thickness of the coating determines the spacing between adjacent elongate nanoparticles and, consequently, the diffraction effect achieved.

A ligand with a sulphur atom at one end and a siloxal group at the other can be used to attach itself to the gold surface of the elongate nanoparticle via the sulphur atom. The distal end of the ligand is then polymerized via a sol-gel reaction to produce a glassy shell around the gold nanoparticle core. The thickness of this shell is easily controlled and so different grating periods are attainable.

Advantageously, grating structure produced according to this technique are totally shielded from their immediate environment and further more behave in the same manner as silica. This enables the convenient orientation of the elongate nanoparticles via the presence of a static electric field.

5 Although the previously described structures have included nanoparticles located in the outer layers of the substrate 2, it is of course possible to locate the nanoparticles elsewhere within the substrate. As shown in Figure 12, an authentication device based upon the optical properties and effects of nanoparticles may be created in which the nanoparticles are centrally located
10 within the substrate 2, providing a window is located in the opacifying layer 45 or 46 for viewing of these optical effects.

The use of acoustic or audio waves to elucidate nanoparticle size may also be used in the context of the present invention. In this case, the inclusion of nanoparticles at any convenient location within the substrate 2 results in an
15 authentication device which does not require visual access to the location within the substrate 2 at which the nanoparticles are held. The authenticity of the security document can be verified by observation of the response to the acoustic waves and verification that the response corresponds to that of an object containing nanoparticles of the size expected to be within that security document. In this
20 case, low concentrations of nanoparticles may be incorporated into banknote film, each denomination having different sized nanoparticles. Authentication and denomination are determined by measuring the different responses to the exciting audio frequency.

The spectra shown in Figure 4 may be achieved without a specific
25 orientation of the longitudinal axes of the nanoparticles. Accordingly, in authentication devices based upon this optical effect, the nanoparticles may easily be formed in the substrate 2 or subsequently located in an outer layer of the substrate by a variety of techniques. For example, the particles may be supported on a transfer foil or film and a heated die is used to press the transfer film to the
30 outer layer of the substrate and so transfer the nanoparticles into the outer layer of the substrate.

In those embodiments of the invention where the longitudinal axes of elongate nanoparticles are required to be aligned, various alignment techniques may be used.

For example, the nanoparticles may be formed in one or more layers of the substrate, and heat applied to at least a first portion of the layer so that the nanoparticles are free to orient themselves. An external field, such as an electric, magnetic, electromagnetic, or mechanically induced stress field, may then be applied so as to orient the nanoparticles in one or more desired directions. The layer may then be allowed to cool so as to fix the orientation of the nanoparticles.

10 In another example, as shown in Figure 14, the nanoparticles may be oriented in a uniform direction on a transfer film or foil. The aligned elongate nanoparticles are then transferred onto the substrate by an embossing technique. Preferably, they are transferred from the release film, although in other embodiments the film may be perforated by the die and also transferred onto the substrate, thereby forming a protective layer of the nanoparticles. The transfer process also embosses the

15 substrate. In this case, the die has a saw-tooth pattern and again various components of an image have their saw-tooth patterns arranged at different angles relative to each other. The profile of the die in this case is much greater than the length of the elongate nanoparticles. Techniques for achieving alignment of the

20 elongate nanoparticles include the use of surface tension, static electricity, magnetic fields and entropic forces. In addition, stretching, the use of static or periodically changing EM fields and self-assembly may be used as ways of orienting the particles.

Alternatively, as illustrated in Figure 15, the elongate nanoparticles may be deposited into pores formed in the outer layer of the substrate. The nanoparticles

25 may be synthesized according to this technique by anodizing the polymer outer layer of the substrate to produce uniform pores in the polymer spaced at regular intervals. The anodizing conditions determine the pore diameter and density. The material used to produce the elongate nanoparticles, such as silver or gold, may

30 then be electrodeposited into the pores. The electrodeposition time period determines the length of the longitudinal axis of the nanoparticle in the pore.

In those embodiments of the invention where the longitudinal axis of the elongate nanoparticles is required to be at an angle to the plane of the security document, the substrate 2 may be exposed to an energy source S whilst the security document is oriented at an angle other than perpendicular to the direction of a beam from the energy source. The tracks thus left in the substrate are therefore oriented at that angle to the normal. The tracks are then able to be used directly as pores for electrodeposition or may be etched to increase their dimensions prior to electrodeposition.

In yet another example, at least a first outer surface of the substrate may be coated with a layer containing spherical nanoparticles, and heat then applied to the layer to allow the spherical nanoparticles to self assemble into a concatenated series. Heat may be applied to the layer as a whole, or to one or more selected portions of the layers. Concatenated series of nanoparticles, or "beads-on-a-string", may thus be created in each of the selected portions. The aspect ratio of the nanoparticle structures may be controlled by the temperature and duration of the heating.

It will be appreciated that various modifications and alterations may be made to the embodiments of the present invention described above without departing from the spirit or scope of the present invention.

The nanoparticles may be used to incorporate covert, machine readable structures into the security document of the present invention. Such structures take advantage of the spectroscopic signals that are unique to nanoparticles, and include narrow bandwidth photoluminescence, polarised photoluminescence, surface enhanced Raman effects, acoustic and photoacoustic effects, magnetic effects and the like.

It will be appreciated that a combination of nanoparticles homogeneously or otherwise distributed within one or more layers of the substrate may be used in the invention. Such a combination would allow the incorporation of multiple nanoparticle effects in a single security document.